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Comment on "About the calculation of exchange coupling constants using density-functional theory: The role of the self-interaction error" [J. Chem. Phys. **123**, 164110 (2005)]

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The energy differences between states of different spin multiplicities play a central role in the interpretation of magnetic properties of organic diradicals, magnetic molecular complexes, and magnetic solids, since these energy differences can be related to the energy spectrum of a model spin Hamiltonian and therefore provide estimates of the parameters (magnetic coupling constants) defining these model Hamiltonians.¹ In molecular systems these energy differences can be directly computed using accurate *ab initio* methods, such as configuration interaction (CI) yielding wave functions in which the relevant spin symmetries (defined by the square of the total spin and its z component, S^2 and S_z) are properly imposed.²⁻⁴ In the case of solid state systems a different procedure is applied because almost universally band structure calculations rely on the use of an effective one-particle picture in which spin symmetry cannot, in general, be imposed. In the latter cases, a mapping procedure can be used by employing the energy differences between the ferromagnetic and broken symmetry antiferromagnetic solutions obtained in the appropriate supercell.⁵⁻⁷ These energy differences are related to the energy spectrum of the appropriate model spin Hamiltonian which, in this case, is the Ising model because only S_z is defined. The broken sym-

metry (BS) solutions can be obtained using either spin-unrestricted Hartree-Fock (UHF) or any of the exchange-correlation potentials within the spin-unrestricted Kohn-Sham (UKS) approach to density functional theory (DFT). In this way, UKS-DFT can be used to extract magnetic coupling constants either in molecules or solids but it is important to realize that, since spin symmetry is broken, a suitable procedure is needed to relate computed energy differences to magnetic coupling constants. The mapping procedure to the appropriate spin Hamiltonian outlined above fulfills this requirement and is consistent with the methods proposed earlier to study the atomic and molecular multiplets^{8,9} and magnetic coupling constants.^{10,11} Essentially, all these procedures are based on the fact that the broken symmetry solution is a mixture of two (or more) spin states and the desired energy splittings are obtained by spin projection or by the sum rule.⁹ Nevertheless, one must be aware of the well known very strong dependence of the energy difference with the chosen exchange-correlation functional, which goes from severe underestimation for the Fock exchange only functional to a huge overestimation for local density approximation (LDA), so mixing Fock and DF exchange can provide any beforehand decided result.

In a recent paper, Ruiz *et al.*¹² compare the numerical results for the magnetic coupling constants obtained for H–He–H and related model systems and investigate the effect of the self-interaction error (SIE). These authors find that the full CI (FCI) value for the magnetic coupling constant is reproduced, either by the energy difference between the high-spin and the broken symmetry states without spin projection provided that the SIE is not removed or by the energy difference with appropriate spin projection if the SIE is removed. Their explanation of this result is that in the projected broken symmetry DFT calculation without SIE corrections, the nondynamical electron correlation is taken into account twice: once via the mapping onto the pure spin symmetry state and once via the exchange part of the density functional. However, this statement lacks a firm theoretical basis. Indeed, as it has been found by Polo *et al.*¹³ and Cremer *et al.*,¹⁴ the SIE of the exchange functional simulates nondynamic electron correlation provided that single determinant spin-restricted density functional theory (RKS-DFT) calculation is carried out. However, in the case of a broken symmetry spin unrestricted calculation, the SIE correction simulates predominantly the effect of dynamic electron correlation, especially in the case of weakly coupled magnetic centers.¹⁴

The results by Ruiz *et al.*¹² do provide evidence that in broken symmetry DFT calculations the spin projection has a considerable effect on the energy and thus they provide indirectly evidence that spin projection is unavoidable or, in other words, that the broken symmetry solution is a mixture of different spin states as argued in several papers.⁵ However, Ruiz *et al.* suggest taking the energy of the broken symmetry solutions as that of the open shell singlet. They observe that a “procedure that gives excellent computational results is to consider that the energy of the broken symmetry solution already contains the nondynamical correlation contributions introduced by the SIE correction and therefore employ the nonprojected approach.” As discussed above, this conjecture lacks a firm theoretical basis. Moreover, it is also incorrect from a purely numerical point of view, because, for all systems studied by Ruiz *et al.*¹² the best performer in the unprojected case is the B3LYP functional, where the effect of the SIE has already been reduced (compared to its pure density functional analog BLYP) due to the mixture with HF exchange. This means that an implicit fine-tuning of the SIE correction is already present in their numerical procedure.

Since correcting for the SIE in real systems is extremely difficult, the procedure suggested by Ruiz *et al.* may potentially lead to a convenient numerical recipe that reduces the strong dependence of the calculated magnetic coupling constants on the choice of exchange-correlation functional and may be useful to unravel magnetostructural correlations. However, although SIE-free potentials are becoming available,¹⁵ the SIE is inherent to all approximate exchange-correlation potentials currently used in standard KS-DFT calculations. Hence, it affects the results obtained using the spin polarized implementation of the Kohn-Sham (KS) procedure as well as those obtained using the KS implementations in which spin symmetry is properly imposed. These procedures are already available¹⁶ and have been recently applied to

compute magnetic coupling constants.¹⁷ In the latter case, there is no reason to carry out the spin projection simply because the reference system has a defined value for both S^2 and S_z and still the results are affected by the SIE. Therefore, one point of the line of reasoning of Ruiz *et al.* is not correct and the source of misunderstanding comes from improperly mixing the concept of SIE with that of spin symmetry.

The underlying problem with this discussion is whether the current implementations of DFT based on the KS approach do or do not require the imposition of spin symmetry. This is an important issue because it has serious implications in all open shell systems and, in particular, in solid state physics. However, while invoking the adiabatic connection formulation of the KS theory¹⁸ to link the fully interacting and noninteracting systems, one should realize that the Hamiltonian operator for all intermediate coupling strengths, $0 \leq \lambda \leq 1$, commutes with the total spin operator. Therefore, the solution to the exact KS problem must obey proper spin symmetry. In practical implementations of the KS method, spin symmetry can be imposed beforehand on the solution of the KS equations or, if an approximate solution that breaks spin symmetry is obtained, proper spin symmetry can be restored afterwards. The former approach is implemented in a number of practical methods based on a spin-restricted KS formulation, whereas the latter approach is executed in the mapping procedures.

The case of solid state systems merits a further comment since, except for one-dimensional infinite chains, there is no analytic solution for the Heisenberg Hamiltonian. Consequently, it is convenient to use the ferromagnetic and broken symmetry antiferromagnetic solutions and to map them into the Ising Hamiltonian eigenenergies. The same result is obtained if, within the given unit cell, spin projection is carried out. Therefore, mapping procedures such as those proposed much earlier^{8,9} provide a general method to extract magnetic coupling constants that is consistent for molecules and solids. Of course, there are other magnetic properties, such as hyperfine coupling constants, which require spin polarization to be explicitly taken into account.¹⁹ In these cases RKS will not be the appropriate choice.

To conclude (1) the SIE is inherent to all approximate exchange-correlation potentials currently used in the standard KS-DFT calculations irrespective of the approach used to include spin symmetry of the corresponding electronic states; (2) the use of a broken symmetry spin polarized description effectively accounts for a part of the electron correlation, but the SIE of a density functional does not necessarily introduce the missing part of the nondynamic correlation; and (3) the use of mapping approaches or equivalently of spin projection provides a consistent way to extract magnetic coupling constants in molecular systems as well as in solid state magnetic systems.

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